

The Variation with Temperature of the Specific Heat of Sodium in the Solid and the Liquid State; also a Determination of its Latent Heat of Fusion.

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Introduction.

The present paper contains the results of an investigation into the variation, with temperature, of the specific heat of sodium in the solid and the liquid state; also, some determinations of its latent heat of fusion.

Our knowledge of the variations of the specific heat of metals in the region of their melting point is extremely vague and hypothetical, since the methods of investigation commonly employed are only capable of giving the mean value of the specific heat over a considerable range of temperature.

In the present work the range of temperature was approximately $1\cdot5^{\circ}$ and the series of experiments at a specified temperature give the absolute value of the specific heat at that temperature, without any assumption concerning the value at another point. Further, the use of a small temperature range renders possible determinations of the specific heat at temperatures close to the melting point; in fact, determinations were made with the middle point of the range only 2° below the melting point.

The element sodium was chosen for investigation, on account of its low melting point, as well as the ease with which it could be obtained in quantities and of the requisite purity. It was necessary, however, to devise means of preventing oxidation and this was accomplished by enclosing the sodium in a sheath of copper of special form. This copper case further served as a containing vessel for the sodium when in the molten state.

Construction and Filling of the Case.—The enveloping sheath of copper was so designed that in outline and general dimensions it was similar to the blocks of various metals used in a previous work.*

Several attempts were made before the difficulties of construction were satisfactorily overcome. Molten sodium dissolves soft solder (50 per cent. Sn and Pb), consequently cases with soldered seams failed.

A case was constructed of thick copper foil, the seams of the tubes and case being doubled back and closed. This case was filled with molten sodium,

* "The Capacity for Heat of Metals at Different Temperatures," by Dr. E. H. Griffiths, F.R.S., and Ezer Griffiths, 'Phil. Trans.,' A, vol. 213, p. 119 (1913).

and after solidification the bottom was pressed on and soldered, the solder not coming into actual contact with the sodium.

One series of experiments at 0° were performed with this block and it was then discarded, as the seams were not air-tight and the soldered bottom could not withstand high temperatures.

It is worthy of note that the mean value of the specific heat at 0° from this series, namely, 0.2864, agrees very closely with the value 0.2863 obtained from the second block which was used in all the determinations at the higher temperatures. The results of the individual experiments are given in Table V, p. 571.

In fig. 1 is shown the final design of the copper case together with the apparatus used when filling it.

The exterior walls W were made of two spun copper vessels, the circumferential seam SS being silver soldered. The tubes H and T, which were to contain the heating coil and platinum thermometer respectively, were of solid drawn copper tubing, closed at the lower ends. These tubes were silver soldered to the top of the case. A small tube in the bottom at P enables the case to be filled, and this was finally closed by a screw-on cap.

The weight of the case* complete was 150 gm. and its capacity 386 c.c.

The method of filling this case was to melt the sodium *in vacuo* and force the molten sodium into the case under the pressure of the atmosphere, by slowly admitting air to the exhausted enclosure.

The case was fixed under the bell-jar in the manner shown, the thermometer serving as a guide to keep it vertical. Around the outside of the iron vessel K, containing the sodium, was wound a heating coil of nichrome wire, insulated by asbestos paper, the leads being led out through the base. The interior of the bell-jar was connected to a Geryk pump which was set going for some time before the sodium was melted. Care was taken to ensure an unobstructed passage during exhaustion to the air contained in the case, and the figure represents the conditions prior to melting.

On the sodium attaining the molten state, the case slowly sank by its weight, some of the molten metal entering by the tube P. The heating was continued until the inner tube was at a temperature of at least 20° above the melting point, when the pump was stopped and air slowly admitted.

Molten metal from beneath the oxidised surface was forced into the case and the block was thus composed of sodium practically free from oxide. When the metal had solidified, screwing the small cap on P completed the

* The specific heat of copper and subsidiary substances, together with their variation with temperature, had been previously determined, *loc. cit.*

operation. The sodium used for this block was obtained from Kahlbaum, and the case contained 366 grm.

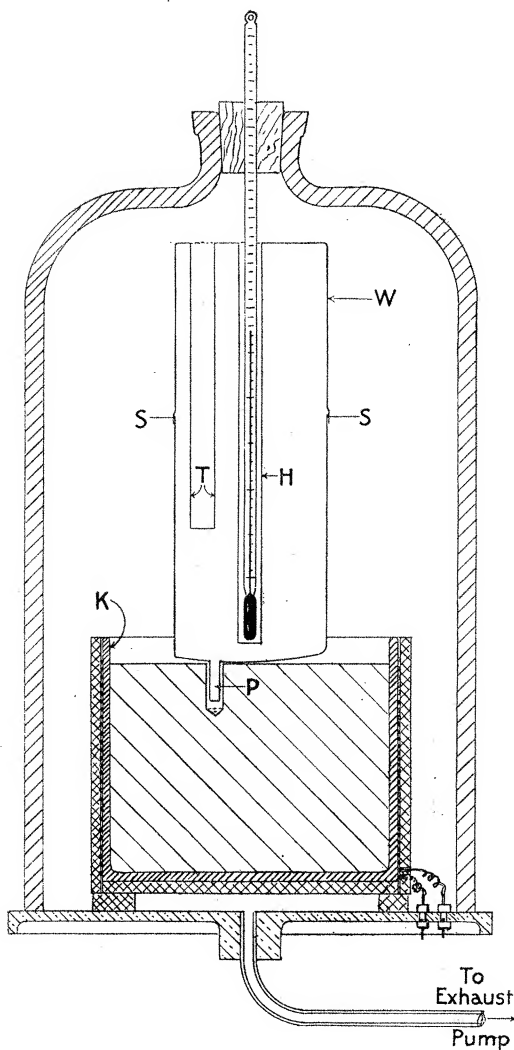


FIG. 1.—Copper case and apparatus for filling.

Determination of the Specific Heat at Various Temperatures.

(a) *Method.*—The method of experiment and the various precautions taken to eliminate sources of error have been described in detail in the paper previously mentioned; here it is only necessary, therefore, to indicate the procedure and the method of reduction, which was practically the same as that previously adopted.

The block was suspended by quartz tubes in an enclosure in a stirred oil tank. The temperature of this tank could be maintained at any desired point for long periods by a controlled electrical heat supply, the oscillations in temperature being of short period and less than $1/50^\circ$ in magnitude.

An experiment was carried out as follows:—

The block was cooled about 3° below the surroundings, the current was then switched on to the heating coil and adjusted until the potential difference at the ends of the coil was balanced against the E.M.F. of a number of standard cells in series.

When the temperature of the block had risen to about 0.7° below the surroundings, observations of temperature and time were commenced, each transit of the temperature across successive bridge wire divisions (approximately $1/14^\circ$) being recorded on a chronograph tape and the observations continued until the temperature had risen to about 0.7° above the surroundings. The time taken to traverse a bridge wire division increased progressively as the temperature rose, on account of the gain or loss due to radiation.

From the data obtained, the values of the rate of rise of temperature, $\partial\theta/\partial t$,* at the corresponding values of θ can be calculated. The value of $\partial\theta/\partial t$ at any point is the sum of two terms: the one due to the electrical supply and the other due to loss or gain by radiation, etc.

When the temperature of the block crosses the surroundings (at θ_N), the loss or gain by radiation vanishes, hence the value of $\partial\theta/\partial t$ at θ_N corresponds to the electrical supply alone, and, having deduced it, the specific heat can be calculated from the well-known expression

$$(ms + MS) \frac{\partial\theta_N}{\partial t} = \frac{n^2 E^2}{JRf},$$

where $\partial\theta_N/\partial t$ is the value of $\partial\theta/\partial t$ at θ_N , and is calculated from the equation of the straight line representing the relation between the observed values of $\partial\theta/\partial t$ and θ .

The temperature θ is measured relatively to the companion differential thermometer fixed in a duplicate block (contained in a similar enclosure immersed in the tank), the temperature of which is not disturbed during a series of experiments. Thus the position corresponding to θ_N on the bridge wire should be the same at all temperatures of the tank if the arrangement was perfectly symmetrical. Actually, the position of θ_N on the bridge wire varied slightly with the tank temperature, the extreme variation from 30° to

* Where $\partial\theta$ is the value of 1 bridge wire in $^\circ$ Pt. at the point and ∂t the time taken to traverse this bridge wire division.

140°, however, only amounted to about 0·03°. At each temperature a series of experiments were performed, in which the rate of energy supply was varied by balancing 4, 5, or 6 standard cells in series.

This variation in the rate of supply affords a severe test of the accuracy of the work, and, moreover, the results of the experiments with different rates afford a means of calculating* the position of θ_N .

To determine θ_N directly requires that the block should have completely settled to the temperature of the surroundings—a process requiring several hours, owing to its asymptotic nature. The calculated position of θ_N generally agreed very closely with the observed value, but where experimental errors at the higher temperatures caused a divergence the observed value was adopted.

The temperature of the tank for each series was determined by a platinum thermometer and reduced to the nitrogen scale.

(b) *Sources of Error.*—In measuring specific heats near the melting point it is necessary to ascertain whether the conditions admit of the fusion of minute portions of the solid by the measured energy supply. An error of this kind would seriously vitiate the results on account of the magnitude of the latent heat of fusion. In the case under consideration, when the electrical supply was on, the inner core of the block around the copper tube containing the heating coil was the region of highest temperature, and a steady gradient existed across the block. An approximate estimate of this gradient can be made by assuming the block to be equivalent to a long cylindrical shell and applying the well-known expression

$$\theta_1 - \theta_2 = \frac{Q \log_e(r_2/r_1)}{2\pi k l},$$

where l , the length of the cylinder, is approximately 15 cm.

r_2 , the radius of the outer surface, is approximately 3 cm.

r_1 , the radius of the inner surface, is approximately 0·55 cm.

k , the thermal conductivity, is not known, but the value of lead, 0·08 (probably an extreme value), may be taken as a rough approximation.

Q , the rate of energy supply, varied from 0·11 to 0·43 calorie per second.

Hence $\theta_1 - \theta_2$ varied from 0·024° to 0·097°.

Thus, with the heaviest rate of energy supply—that due to a potential difference of 6 Cd cells—the difference in temperature across the block did not exceed one-tenth of a degree.

Apart from this estimate, which involves many assumptions, there is strong

* See 'Phil. Trans.,' 1913, p. 149.

internal evidence from the experiments themselves that no perceptible error due to this cause existed, for we should expect that the experiments with the higher rate of supply would be more affected than the slower rate and, consequently, give high values for the specific heat.

Taking the results of the series with the mid-point of the range 2° below the melting point, we have the following values for the specific heat deduced from the different rates:—

0.3260	from the 4 Cd cell rate.
0.3254	„ 5 „
0.3260 (mean)	6 „

The rate of supply in these experiments was as 16 : 25 : 36. Hence the marked increase in the specific heat (see fig. 2) as the melting point is approached is not due to errors of experiment.

Results.

A remarkable feature of the specific heat values in the solid state is their dependence on the nature of the previous heat-treatment of the metal.

Discrepancies which might at first sight be ascribed to errors of experiment were proved to be of real significance by the fact that the specific heat values in the liquid state could be reproduced to within a few parts in 10,000, after the most varied heat-treatment, while differences of as much as 2 per cent. were encountered in the solid state.

The importance of this point was not sufficiently realised in the early determinations and a large number of otherwise excellent experiments have been rendered worthless through lack of attention to the precise nature of the previous heat-treatment.

It was found that a slow cooling of the block from the liquid state produced an “annealed” condition of the metal in which the specific heat corresponding to each temperature was definite and could be reproduced. A comparison of the dates of the determinations in Table I, which summarises the results for the annealed state, will indicate the extent to which concordant results could be obtained on repetition under similar conditions.

For example, on completing the series of August 8, giving the value 0.2953, the block was taken out, heated up to 100° and allowed to cool rapidly in air. The value then obtained for the specific heat was 0.3014. Again heating to 100° , and allowing to cool very slowly, gave the value 0.2953, identical with the value previously obtained for the “annealed” state at the same temperature. Most of the determinations recorded in Table I correspond to a rate of cooling of the block from the liquid state of

certainly less than 4° per hour, which was the rate of fall of the outside tank from 100° to 86° .

Table I.—“Annealed” State.

Temp.	Date.	No. Cd cells.	Specific heat.	Mean.
°				
0	Aug. 28.....	4	0·2835	0·2829
		5	0·2836	
		6	0·2820	
		6	0·2826	
28·82	Aug. 19.....	4	0·2911	0·2910
		5	0·2910	
		6	0·2929	
		6	0·2893	
49·38	Aug. 8.....	4	0·2954	0·2953
		4	0·2952	
		5	0·2951	
		5	0·2955	
		6	0·2951	
		6	0·2955	
49·27	Aug. 16.....	4	0·2946	0·2953
		5	0·2949	
		6	0·2964	
49·07	Aug. 17.....	5	0·2963	0·2950
	Aug. 20.....	5	0·2945	
		6	0·2942	
67·79	Aug. 21.....	4	0·3014	0·3019
		5	0·3037	
		5	0·3018	
		6	0·3010	
		6	0·3018	
79·15	Aug. 22.....	4	0·3083	0·3083
		5	0·3085	
		6	0·3086	
		6	0·3079	
85·65	Aug. 15.....	4	0·3168	0·3171
		5	0·3181	
		5	0·3165	
		6	0·3178	
		6	0·3159	
90·03	Aug. 23.....	4	0·3209	0·3209
		5	0·3208	
		6	0·3208	
		6	0·3210	
95·53	Aug. 24.....	4	0·3260	0·3258
		5	0·3254	
		6	0·3260	

In Table II are summarised the results of a number of determinations of the specific heat after the sodium had been rapidly cooled from the liquid state.

The previous heat-treatment was as follows:—

The block was heated in an oil bath to 130° and then rapidly transferred to a vessel of ice-cold water. This condition of the metal will be termed the “quenched” state in subsequent pages.

The determinations were made starting from the lowest temperature (0° C.) and progressing in steps up to 94°.

It will be observed that the complete series occupied several days and some annealing may have taken place at the higher temperatures. It is now proposed to investigate, by a new method, the changes with time due to slow annealing and also the relationship between crystalline structure and specific heat in the case of other metals besides sodium.

Table II.—“Quenched” State.

Temp.	Date.	No. Cd cells.	Specific heat.	Mean.
0	Aug. 29.....	4	0·2892	0·2870
		5	0·2874	
		6	0·2864	
		6	0·2852	
40·16	Aug. 30.....	4	0·2973	0·2981
		5	0·3002	
		6	0·2953	
		6	0·2992	
		6	0·2983	
68·60	Aug. 31.....	4	0·3024	0·3040
		5	0·3049	
		6	0·3073	
68·60	Sept. 2	4	0·3034	0·3089
		5	0·3320	
		6	0·3038	
82·15	Sept. 3	4	0·3087	0·3200
		5	0·3094	
		6	0·3095	
		6	0·3079	
94·02	Sept. 4	4	0·3195	0·3200
		5	0·3213	
		6	0·3192	
		6	0·3200	

As might be anticipated, the specific heat corresponding to each temperature in the molten state is definite and independent of the previous heat-treatment. The values are collected in Table III. The relation between the specific heat and temperature is practically a linear one over the range of temperature investigated, and it is noteworthy that the temperature coefficient of the specific heat, $-0\cdot00034$ per degree between 100° and 140°, is very similar to the value for mercury, $-0\cdot00030$ between 0° and 40°.

The determinations were not done consecutively, the series at 103° being carried out on July 19, while the adjacent series at 101° were done subsequent to a considerable number of determinations (after various heat-treatments) in the solid state, and it is remarkable that the two values 0.3232 and 0.3234 differ by exactly the quantity required for 2° difference in temperature by the coefficient of decrease in specific heat in the molten state. At higher temperatures the experimental errors were more pronounced, and the mean values of several experiments with each rate were taken.

Table III.—Liquid State.

Temp.	Date.	No. Cd cells.	Specific heat.	Mean.
°				
100.81	Aug. 14	4	0.3237	0.3234
		5	0.3226	
		6	0.3227	
		6	0.3246	
103.09	July 19	4	0.3232	0.3232
		5	0.3232	
		5	0.3232	
		6	0.3221	
		6	0.3242	
117.03	July 20	4	0.3218	0.3217
		5	0.3206	
		5	0.3224	
		6	0.3218	
		6	0.3218	
127.53	July 31 and Sept. 5	4	0.3197	0.3205
		5	0.3205	
		6	0.3212	
138.47	July 30	4	0.3185	0.3189
		4	0.3204	
		5	0.3183	
		5	0.3167	
		6	0.3205	
		6	0.3193	

Fig. 2 represents the results graphically. The relation between the specific heat and temperature in the "annealed" and molten state is shown by the full lines.

The broken line represents the results of the determinations after the sodium had been "quenched." The metal is probably unstable in this state near the melting point, and consequently the specific heat would be a function of time as well as of temperature.

In the early part of this paper reference was made to the fact that experiments were conducted at 0° with two different samples of sodium. As the methods of construction and the quantities involved were different

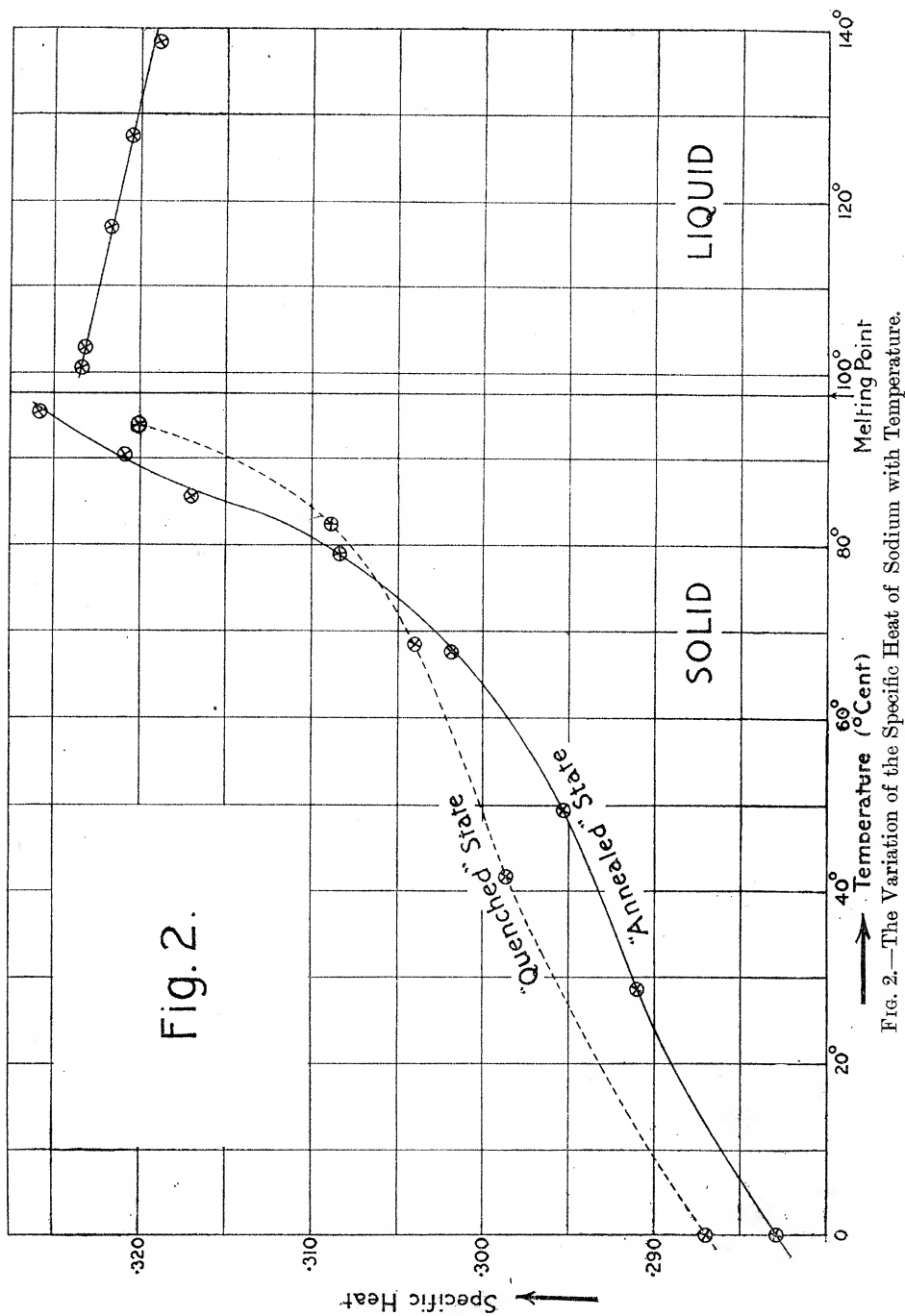


FIG. 2.—The Variation of the Specific Heat of Sodium with Temperature.

in the two cases the results are of importance, inasmuch as they indicate the absence of any serious systematic error. The heat-treatment in both cases was somewhat similar, the sodium being allowed to cool freely in air from the molten state.

Sample A refers to the block constructed with lapped seams and soft solder. This case was filled by pouring in molten sodium from an iron kettle.

Sample B refers to the block constructed from spun copper vessels and filled *in vacuo* with Kahlbaum's sodium.

Table IV.

	Sample A.	Sample B.
Mass of sodium	340.65 gm.	366.04 gm.
„ copper.....	87.54 „	154.3 „
„ soft solder	4.37 „	
Volume of oil around heating coil	8.08 c.c.	8.5 c.c.
Resistance of heating coil	20.634 ohms	20.628 ohms

The values of the specific heat calculated from the various rates are given in Table V.

Table V.

Sample.	Date.	No. Cd cells.	Specific heat.	Mean.
A	April 7	3	0.2861	0.2864
		4	0.2868	
		5	0.2866	
		5	0.2864	
		6	0.2858	
B	June 4	4	0.2864	0.2863
		5	0.2871	
	„ 5	3	0.2862	
		6	0.2855	
	„ 6	5	0.2864	
		6	0.2863	

The mean value of the specific heat from the above two series is intermediate between the values at 0° for the “annealed” and the “quenched” states respectively (see Tables I and II), and it is noticeable that in both cases the sodium had received heat-treatment of an intermediate character. Several determinations were made at temperatures between 88° and 94° after a somewhat similar heat-treatment, and the same feature is common to all, the values falling between the extremes corresponding to the “annealed” and the “quenched” states. However, in the case of two series at 65° and 81° the values were distinctly higher than those corresponding to the “quenched” state; much weight cannot be attached to these two series,

as they were the first performed at the higher temperatures when the thermostat was not working properly.

Determination of the Latent Heat of Fusion.

The following is a brief description of the methods adopted for determining the latent heat of fusion:—The platinum thermometer in the sodium block was disconnected from the differential arrangement used in the specific heat work, and directly connected to a Callendar and Griffiths' resistance bridge. The freezing point was first determined by the cooling curve method, the usual undercooling and superfusion being traced, and the freezing point found to be 97.61° C. The tank temperature was then set and controlled at a temperature of approximately 0.8° below the melting point. The temperature of the sodium block was lowered several degrees below the surroundings, and a heavy rate of electrical supply switched on to the heating coil and maintained constant.

Observations of temperature and time were taken right up to the melting point; near the melting point the rate of rise rapidly decreased to zero. The transition from solid to liquid took from one and a-half to three hours, according to the rate of supply. When the sodium had been converted into the molten state the temperature again rose steadily, and the observations were continued until a sufficient number had been obtained, then the electrical supply was switched off and the cooling curve taken.

From the time-temperature observations in the solid and liquid states it is easy to deduce, graphically or by calculation, the total time required to convert the sodium from solid to liquid, assuming the process to commence and cease sharply at the temperature corresponding to the melting point.

The rate of cooling at various temperatures supplies the data for computing the rate of loss of heat due to radiation, etc., during the time the sodium was melting. Table VI summarises some of the more important data for two experiments done on separate occasions.

A variation of the above method is to determine the total quantity of heat required to raise the temperature of the block from about 90° to 105° .

An experiment by this method, using a 12-cell rate and the surroundings at 96.8° , gave the value 27.7 for the latent heat. The method is not so accurate as the previous one, since the corrections for losses by radiation during the latter part of the experiment become of serious magnitude.

It is interesting to observe that an approximate value of the latent heat can be deduced from the cooling curve alone, without any measurements of energy, provided the thermal capacity of the block and accessories can be calculated from the specific heats.

Table VI.

Mass of sodium = 366.04 gm. Thermal capacity of sodium, case, oil, etc., at these temperatures (calculated from the specific heats) = 143.72 gm.-calories.

	Expt. 1.	Expt. 2.
Number of standard cells balanced	9	12
Resistance of coil for this rate of energy supply* ...	20.6265	20.6132
Deduced time of melting	10,928 secs.	5,978 secs.
Rate of cooling for this temperature.....	0.00035° per sec.	0.00033° per sec.
Latent heat	27.54 gm.-cals.	27.50 gm.-cals.

* It is to be remembered that at this temperature manganin has a negative temperature coefficient of resistance, hence the heating effect of the current lowers the value of the resistance.

From the time-temperature curve the total time taken to pass from liquid to solid can be deduced. From the observed values of the rate of cooling at various temperatures, the loss of heat per second at the temperature of the melting point can be calculated, and this, together with the thermal capacity at various temperatures, is all that is necessary for an estimation of the latent heat.

But one experiment was made by this method, as the observations were very tedious, the process of solidification alone occupying $6\frac{1}{2}$ hours and the complete experiment necessitated the counting of a tape 800 yards long, with about 29,000 seconds marks.

The duration of the experiment could be shortened by increasing the difference in temperature between the surroundings and the melting point, which in this case amounted to only 8°, but this would render the accurate determination of the rate of cooling at the higher temperatures more difficult.

The value deduced for the latent heat by this method was approximately 27.1 gm.-calories.

The mean value from the first method is undoubtedly the most reliable and the latent heat may be taken as 27.52 gm.-calories.

My thanks are due to Dr. Griffiths, not only for suggestions connected with this inquiry, but also for practical assistance in certain of the experiments, and to my brother, Edgar A. Griffiths, for constructing the cases and for constant help with the observations.

Note.—This investigation must be regarded as an extension of that already published in 'Phil. Trans.,' p. 119, 1913, and as that investigation is now being pursued to lower temperatures, a discussion of the theoretical bearing of the work is deferred until the completion of the low-temperature series.

Note on the Difference in Density between the Annealed and Quenched States of Sodium.

After the preceding paper was written it was suggested that the densities in the two solid states should be ascertained in order to find whether the following generalisation was true :—

That the denser state has the smaller specific heat.

The density determinations here referred to should be regarded as of a preliminary nature only, and the following brief description indicates the method by which they have been obtained.

Two similar spherical glass vessels (with small openings) are suspended in an oil bath from the arms of a short-beam balance.

Both vessels contain sodium, the one annealed and the other quenched, equilibrium being obtained by adding small weights to the lighter side. The annealed specimen is then heated up beyond the melting point and quenched whilst the specimen previously quenched is annealed.

Equilibrium is again obtained, and from the difference in the weights the change in density consequent on change of heat-treatment can be deduced; the cycle of operations being repeated as often as desired.

All the experiments indicate that sodium in the quenched state is *less dense* than in the annealed state; and further, they consistently indicate that this difference is of the order of 1 part in 7000.

It may be remarked that there is no difficulty in measuring changes of density of this amount by means of the differential method employed; in fact, a difference of one-tenth this magnitude can be measured.

The experimental difficulty is to prevent chemical action between the sodium and any traces of moisture present in the oil.

A point which requires consideration in connection with such minute differences in density is the possibility of the formation of small cavities in the metal when quenching. Cavities filled with the oil under which the manipulations are performed would, however, have no influence on the measurements.

It is of interest to note that if we regard the difference of 1 part in 7000 in the density as being due to the presence of varying amounts of an amorphous modification cementing the crystals together, then the quenched state contains at least 0·3 per cent. more of the amorphous form than the annealed state. This is probably an underestimate, since the value of the density of molten sodium at 98° has been assumed for the amorphous form.—*January 21, 1914.*
